Synthesis of Zirconium and Hafnium *ansa*-Metallocenes *via* Transmetalation of Dielement-Substituted Bis(cyclopentadienyl) and Bis(indenyl) Ligands

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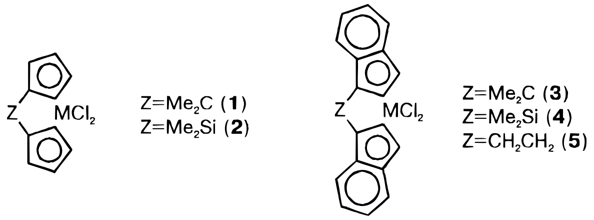
Distannylated bis(cyclopentadienyl) and bis(indenyl) ligands react with $ZrCl_4$ and $HfCl_4$ to give the corresponding *ansa*-metallocenes in high yield. It was shown that the racemic forms of *ansa*-metallocenes could be prepared from the racemic forms of starting dielement-substituted bis(cyclopentadienyl) ligands.

Chiral *ansa*-zirconocenes and hafnocenes are under active investigation as a new generation of stereospecific catalysts for the (co)polymerization of α-olefins.[1,2] Very often the synthesis of such complexes is not straightforward. Usually the procedure involving interaction of metal tetrahalides with the dilithium salts of the corresponding ligands is used.[3] Dipotassium[4] salts have been used as well as the starting material, with some improvement in reaction yields but at the expense of selectivity. These protocols have some disadvantages, such as low yields, the requirement of high-dilution conditions (that is, large amounts of solvents), and, quite often, poor selectivity for the desired racemic isomer.

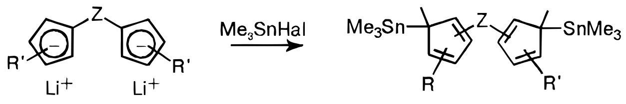
Given the rapid evolution of the use of zirconocene-based catalysts in industrial polymerization processes, the elaboration of a high-yield, diastereoselective and general synthetic method for *ansa*-metallocenes would be of great practical relevance. We supposed that distannylated bis(cyclopentadienes) and in some cases disilylated bis(cyclopentadienes) could be very promising starting materials for their preparation. Some examples of such an idea were published recently.[5]

The main reasons for our suggestion are as follows: (i) Simple stannylated cyclopentadienes are, in fact, very accessible substances and could be produced from lithium cyclopentadienyl salts in almost quantitative yield. (ii) Stannylated and some other element-substituted cyclopentadienes readily react with metal halides, including Zr and Hf halides, to give the corresponding cyclopentadienyl derivatives.[6] (iii) Stannylated cyclopentadienes are relatively stable substances toward oxygen and moisture.

Chart 1



Scheme 1



To test this hypothesis, we carried out the synthesis of some *ansa*-metallocenes. As model compounds, we have chosen two simple *ansa*-bis(cyclopentadienyl) complexes comprising single carbon (**1**) and silicon (**2**) bridges and three *ansa*-bis(indenyl) derivatives with carbon (**3**), silicon (**4**), and dimethylene (**5**) bridges (Chart 1).

Distannylated bis(cyclopentadienes) are easily obtained by the reaction of dicyclopentadienyl derivatives of alkali metals with the proper trialkyltin halide.[7] Monitoring of this reaction by means of ^{1}H NMR spectroscopy shows that the yields of the distannylated product are practically quantitative. No byproducts can be detected.[8]

The boiling points of distannylated bis(cyclopentadienes) (Scheme 1) are very high, so it is difficult to distill them. Therefore, usually we did not isolate these compounds but rather used them *in situ*.

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(8) In the case of bis(indenyl) derivatives, 1:1 *rac*/*meso* mixtures of distannylated products were detected.

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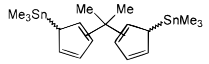
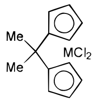
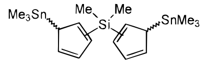
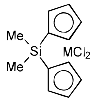
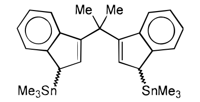
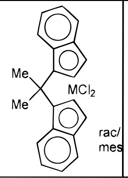
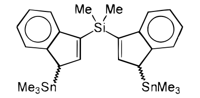
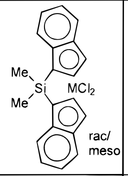
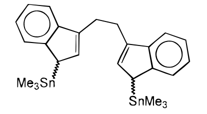
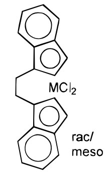
S0276-7333(96)00435-9 CCC: $14.00

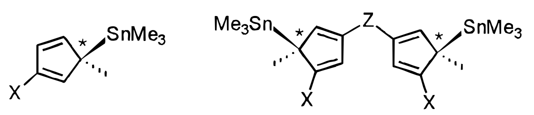
Table 1. Synthesis of the Model *ansa*-Metallocenes through Distannylated Ligands

Starting material	product	M in complex	Yield		Ref.
			in THF	in toluene	
		Zr Hf	7	94 96	15 15
		Zr Hf	8	94 93	11 11
		Zr Hf	4	46 44	12 16
		Zr Hf	7	42; rac- 41; rac-	17 12
		Zr Hf	11	45; rac- 43; rac-	14 18

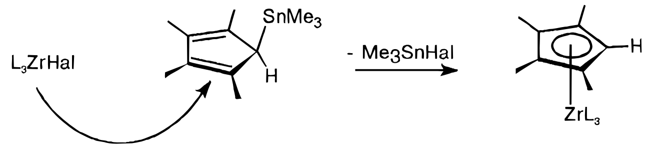
We investigated the reaction of distannylated bis(cyclopentadienes) with zirconium and hafnium tetrachlorides. It was shown (see Table 1) that in THF the yields of the *ansa*-metallocenes are not high, likely because the coordination of metal chlorides by THF and, thus, deactivation of MCl_4.

The use of the toluene as a solvent, on the contrary, allowed us to isolate *ansa*-compounds with total yields (*rac* + *meso*) in the range 90–95%. The rate of the process was faster for the cyclopentadienyl derivatives. The slowest reaction was the formation of *ansa*-metallocenes **3** that contain the $-Me_2C-$ bridge. Bis(indenyl) derivatives **3**–**5**, obtained by our method, consist of equimolecular mixtures of *rac* and *meso* isomers. The racemic forms are less soluble in organic solvents and can be isolated by recrystallization. The final yields of pure racemic forms were at least 40–45%.

Chart 2



Scheme 2



It is well-known that stannylated as well as some other cyclopentadienes and indenes can undergo sigmatropic shifts of the σ-bonded R_3Sn group.[9] It is very important that these shifts are suprafacial and the tin atom is located on one determined side of the cyclopentadienyl ring. So stannylated unsymmetrically substituted cyclopentadienes and indenes are chiral molecules (see Chart 2; the chirality is of the planar type, similar to that of 1,2- and 1,3-disubstituted ferrocenes).

Therefore distannylated, unsymmetrical bis(cyclopentadienes) and bis(indenes), like the corresponding *ansa*-metallocenes, are obtained as *rac*/*meso* diastereoisomers. The same is true for other element-substituted cyclopentadienes and indenes, *e.g.* for germylated and silylated derivatives. If one takes into consideration that metal halides react with stannylated cyclopentadienes with inversion of configuration (Scheme 2),[6d] the reaction of $ZrCl_4$ with one diastereoisomer of distannylated ligand should lead to a single diastereoisomer of the corresponding *ansa*-metallocene; the *syn* ligand isomer yields the *meso*-*ansa*-metallocene, and the *anti*-ligand isomer yields the *rac*-*ansa*-metallocene.

To test this hypothesis we investigated the interaction between $ZrCl_4$ and two pure racemic forms of dielement-substituted bis(indenyl) ligands, *i.e.* 1,2-bis((trimethylsilyl)inden-1-yl)ethane (**6**-*rac*) and 2,2-bis(3-methyl-3-(trimethylstannyl)inden-1-yl)propane (**7**-*rac*) (**6**-*rac*) and **7**-*rac* were isolated by recrystallization from the 1:1 *rac*/*meso* mixtures). It was found that both processes lead to the formation of mainly racemic *ansa*-metallocenes, and in the case of **7** the stereochemical as well as the chemical yields are almost quantitative (Scheme 3).

Therefore, it is confirmed that pure racemic *ansa*-metallocenes can be synthesized by starting from racemic stannylated ligands.

Experimental Section

General Methods. All solvents and the reagents were obtained from commercial sources and purified as requested. Starting bis(cyclopentadienes)[10,11] and bis-indenes[12–14] and their dilithium salts were prepared by the usual methods. Synthetic procedures were performed using Schlenk techniques.

^1H- and ^{13}C-NMR spectra were registered with Varian XR-300 and Varian XR-400 spectrometers. Chemical shifts were referenced relative to residual ^1H impurities in deuterated solvents.

Synthesis of Group 4 *ansa*-Metallocenes from Dilithium Derivatives. General Procedure. To a suspension of the dilithium derivative of the "bis(cyclopentadienyl)-type" ligand (50 mmol in 250 mL of ether) was added 110 mmol of Me_3SnCl at −40 °C. The reaction mixture was then warmed to room temperature. The resulting yellow solution was

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(16) $Me_2CInd_2HfCl_2$ (**3b**) was prepared like **3a**.[12] ^1H-NMR (CD_2Cl_2, 30 °C): δ 7.85 ("d", 2H), 7.52 ("d", 2H), 7.30 (m, 2H), 7.06 (m, 2H) {C_6 of indene} 6.64 (d, $J = 3, 4$ Hz, 2H), 6.18 (d, 2H) {C_5 of indene}, 2.40 (s, 6H, $>CMe_2$). Anal. Calc for $C_{21}H_{18}Cl_2Hf$: C, 48.53; H, 3.49. Found: C, 48.26; H, 3.55.

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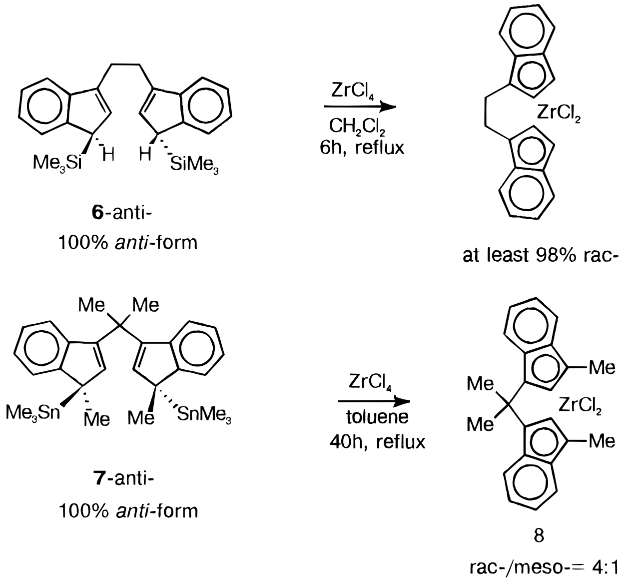
Scheme 3



isolated and evaporated. A suspension of 50 mmol of MCl_4 (M = Zr, Hf) in 200 mL of toluene was then added, and the reaction mixture was stirred for 4 h at 80 °C. Then toluene and R_3SnCl were removed at 80−90 °C and ~1 Torr. The solid residue was recrystallized or washed by the appropriate solvent. The yields of the products are given in the Table 1.

Synthesis of Racemic Forms of Dielement-Substituted Bis(indenes) 6-*rac* and 7-*rac*. *rac*-1,2-Bis(3-(trimethylsilyl)inden-1-yl)ethane (6-rac). A 5.40 g (50 mmol) amount of Me_3SiCl was added dropwise at −40 °C to a suspension of 5.81 g (21.5 mmol) of dilithio-1,2-bis(indenyl)ethane in 100 mL of Et_2O. The solution was isolated and evaporated, and the residue was recryctallized from pentane. The yield of **6**-*rac* is 3.20 g (37% based on all ligand).

^{1}H-NMR (C_6D_6, 30 °C): δ 7.60 ("d", 2H), 7.53 ("d", 2H), 7.38 ("t", 2H), 7.30 ("t", 2H) {ABCD of indene}, 6.41 (d, 2H, =CH−), 3.37 (bs, 2H, C_5 ring), 3.17 (bm, 4H, $-CH_2CH_2-$) 0.027 (s, 18H, $-SiMe_3$). Anal. Calc for $C_{26}H_{34}Si_2$: C, 77.54; H, 8.51. Found: C, 77.22; H, 8.41.

***rac*-2,2-Bis(3-methyl-3-(trimethylstannyl)inden-1-yl)propane (7-*rac*).** A solution of the *dilithium salt* of 2,2-bis(indenyl)propane (10.2 g, 35.9 mmol) in 50 mL of THF was treated by MeI (5 mL, excess) at −30 °C. The mixture was then warmed to room temperature, stirred 30 min at this temperature, and washed with water (10 mL, twice). The resulting solution was evaporated, and the residual brown oil was dried *in vacuo*, dissolved in 100 mL of Et_2O + 10 mL of THF, cooled to −20 °C, and then treated with 33 mL of 2.2 M *n*-BuLi in hexane. The dilithium salt of 2,2-bis(3-methylinden-1-yl)propane•2THF (12.3 g, 75%) was separated and washed.

A 10.2 g (35.9 mmol) amount of the *dilithium salt* of 2,2-bis(indenyl)propane in 50 mL of THF was treated with MeI (5 mL, excess) at −30 °C. The mixture was allowed to warm to room temperature, and solvent was removed. The residue was poured into 100 mL of H_2O/100 mL of Et_2O, the organic layer was separated, and the solvent was removed under reduced pressure. The resulting brown oil was dried *in vacuo*, dissolved in 100 mL of Et_2O + 10 mL THF, cooled to −20 °C, and then treated with 33 mL of 2.2 M *n*-BuLi. A 12.3 g (75%) amount of the dilithium salt of 2,2-bis(3-methylinden-1-yl)propane•2THF was isolated.

^{1}H-NMR (THF-d_8, 30 °C): δ 7.42 (d, 2H), 7.10 (d, 2H), 6.26 (t, 2H), 6.18 (t, 2H), 6.47 (s, 2H), 2.33 (s, 6H), 1.90 (s, 6H).

A suspension of 1.11 g (2.43 mmol) of dilithio-2,2-bis(3-methylinden-1-yl)propane in 50 mL of Et_2O was treated at −40 °C with 5 mmol of Me_3SnCl. The solution was decanted and evaporated, and the residue was recrystallized from pentane. The yield of **7**-*rac* is 0.673 g (44% based on all ligand).

^{1}H-NMR (toluene-d_8, 30 °C): δ 7.55 ("d", 2H), 7.23 ("d", 2H), 6.95 (m, 4H) {ABCD-indenyl}, 6.53 (s, 2H, >CH, C_5 ring), 1.84 (s, 6H, $>C(CH_3)_2$), 1.64 (s, 6H, $-CH_3$), −0.11 (s, 18H, $-Sn(CH_3)_3$). Anal. Calc for $C_{29}H_{40}Sn_2$: C, 55.64; H, 6.44. Found: C, 55.57; H, 6.50.

Interaction of 6-*rac* with $ZrCl_4$. A 3.2 g (8 mmol) amount of **6**-*rac* was dissolved in 20 mL of CH_2Cl_2, treated by 1.85 g (8 mmol) of $ZrCl_4$, and heated until reflux for 6 h. Then the solvent was removed, with and the residual solid was recrystallized from THF. The yield of pure (EBI)$ZrCl_2$ was 98%.[14]

Interaction of 7-*rac* with $ZrCl_4$. A 0.67 g (1.1 mmol) amount of **7**-***rac*** was dissolved in 20 mL of toluene, treated with 0.25 g (1.1 mmol) of $ZrCl_4$, and heated until reflux for 40 h. After conventional workup the yield of **8** was 54% (the *rac*/*meso* ratio was 4:1).

^{1}H-NMR (CD_2Cl_2, 30 °C; δ): *rac* form, 7.64 ("d", 2H), 7.42 ("d", 2H), 7.22 (m, 2H), 6.96 (m, 2H) {C_6 ring}, 5.83 (s, 2H, C_5 ring), 2.30 (s, 6H), 2.28 (s, 6H) {−Me}; *meso* form, 7.79 ("d", 2H), 7.37 ("d", 2H), 7.06 (m, 2H), 6.84 (m, 2H) {C_6 ring}, 5.53 (s, 2H, C_5 ring), 2.67, 2.07 (s, 2 × 3H, $>CMe_2$), 2.36 (s, 6H, −Me). Anal. Calc for $C_{23}H_{22}Cl_2Zr$: C, 59.98; H, 4.81. Found: C, 59.76; H, 4.79.

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